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Hopping conduction in pure and doped poly(vinyl-alcohol)

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The electrical characteristics of polymer is of considerable importance due to the need of conducting polymer materials with good mechanical and electrical properties. Attention has been focused on poly(vinyl-alcohol) (PVA) for more than 30 years because its unique chemical and physical properties as well as industrial application (Sakurada 1985). A large number of experimental results have been reported in literature, but it has been always diffcult to give a proper explanation of the experimental results with the existing theoretical models. Investigation has so far been made mainly on the electrical conductivity of pure and doped PVA. Several authors attribute the conduction to be due to ionic and electronic hopping process (Oster and Herspring 1968, Porrini 1973, Flaming 1970, Hill 1967 and Eliott 1984), but most of them does not confirm this by applying an appropriate theoretical model. This work deals with the application of 'hopping model' to some published experimental data (Basha and Aminen 1987, Basha and Badawy 1986, Jain *et al* 1978).

For materials containing good concentration of defects, electron transport can take place via such defects. The transfer of electrons between sites localized at different positions in space is commonly termed as 'hopping'. Impurity conduction occurs due to the hopping of electrons between the filled localized states and those states which are empty. The following equations used to describe the hopping conduction in insulators and semiconductors (Eliott 1984).

$$\sigma=\frac{e^2}{6}R^2\nu_0 \exp(-2\alpha R-A/k_\beta T)$$

$$=\sigma_0 \exp[-A/T^{1/4}] \quad (1)$$

$$A=2.1(\alpha^3/k_\beta N(E_F))^{1/4}, \quad (2)$$

where α^{-1} is the localized length, k_β the Boltzman constant, T is the absolute temperature, R is the spatial separation between two localized states

and $N(E_F)$ is the density of state at the Fermi level. The exponent A is used to extract the value for $N(E_F)$. We put $\alpha^{-1}=10$ Å. All other parameters have usual meanings (Eliott 1984).

Figure 1 shows the plot of log σ vs $T^{-\frac{1}{4}}$ for sample of PVA+10% $NiCl_2$, we observe that the $T^{-\frac{1}{4}}$ temperature dependence seem to fit two different stright lines one for $T < T_0$, and the other for $T > T_0$, where T_0 is the glass transition temperature. Similar plots could be drawn for other composites. Table 1 represent the values of the hopping conduction parameters for our

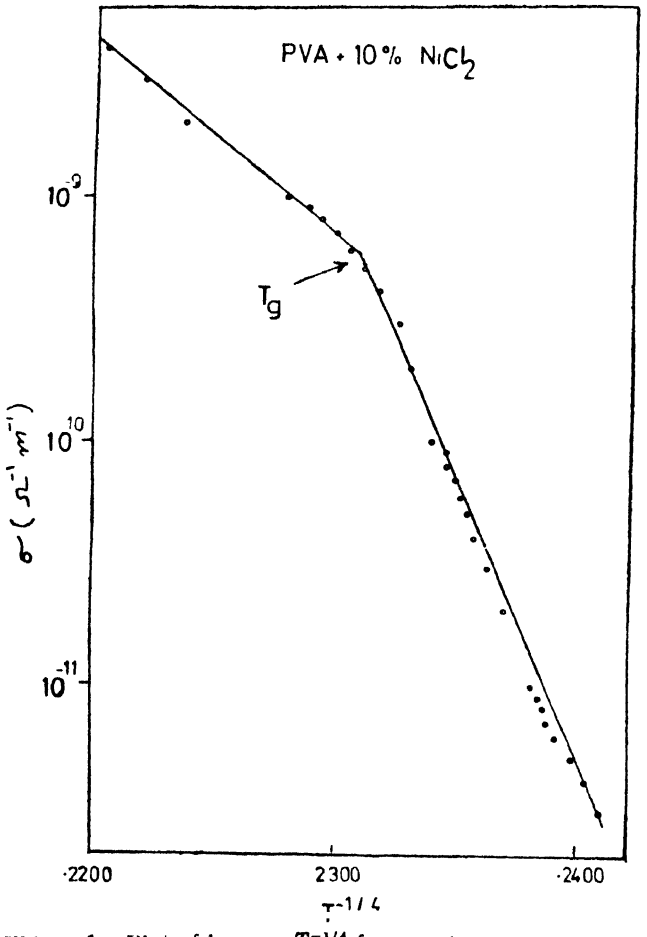

Figure 1 Plot of log σ vs $T^{-1/4}$ for sample PVA+10% $NiCl_2$.

samples at two different temperatures. We notice from the table that the average hopping distance (R) at first increases by increasing $NiCl_2$ concentration, and then decreases by increasing $NiCl_2$ contents. This enables us to suggest that there is no chemical bond formation between PVA and $NiCl_2$. Thus the $NiCl_2$ does not share in hopping conduction of PVA matrix but make another

separate matrix which contributes separatey to the conductivity. Therefore, the hopping mechanism appears to be a resultant phenomena.

Figures 2 and 3 represent the plots of log σ vs $T^{-\frac{1}{4}}$ for samples PVA+10% C and PVA+50% C. The values of R and A estimated at two different temperatures are shown in Table 1. We observe that for all samples, except PVA+50% C, $T^{-\frac{1}{4}}$ dependence seem to fit two different straight line. From Figure 3 it is clear that the conduction for PVA+50% C is not primarily

Table 1. Conduction parameters for pure and doped poly (vinyl-alcohol.)

Temperature (°K)	Sample	A	R (Å)
303	PVA (pure)	198	172
	PVA+10% $NiCl_2$	225	197
	PVA+30% $NiCl_2$	163	143
	PVA+80% $NiCl_2$	140	122
403	PVA (pure)	77	63
	PVA+10% $NiCl_2$	81	67
	PVA+30% $NiCl_2$	79	65
	PVA+80% $NiCl_2$	65	53
303	PVA (pure)	285	249
	PVA+10% C	285	249
	PVA+30% C	68	60
403	PVA (pure)	114	108
	PVA+10% C	26	21
	PVA+30% C	101	83
323	PVA (pure)	234	211
	PVA+25% PVAc	376	327
	PVA+50% PVAc	202	176
	PVA+75% PVAc	383	334
	pure PVAc	119	102
373	PVA (pure)	93	79
	PVA+25% PVAc	177	148
	PVA+50% PVAc	122	102
	PVA+75% PVAc	57	48

due to hopping type mechanism. This may be attributed to the sample lying above the percolation thershold, and the conduction is believed to be mainly

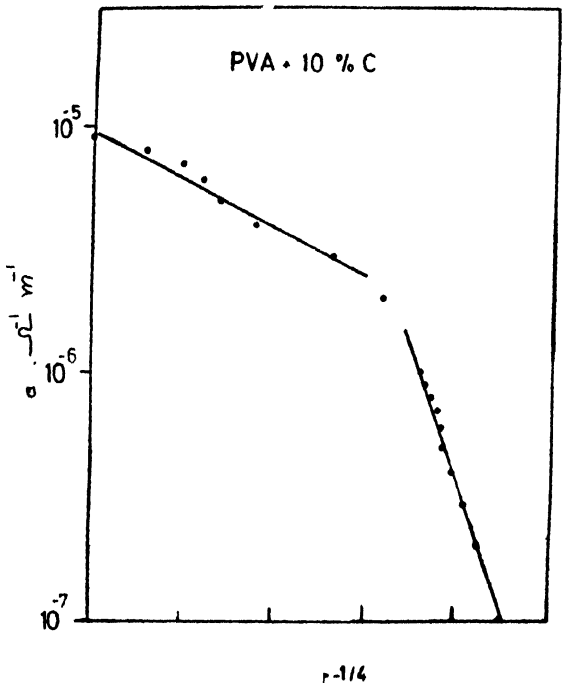

Figure 2. Plot of log σ vs $T^{-1/4}$ for sample PVA+10% C.

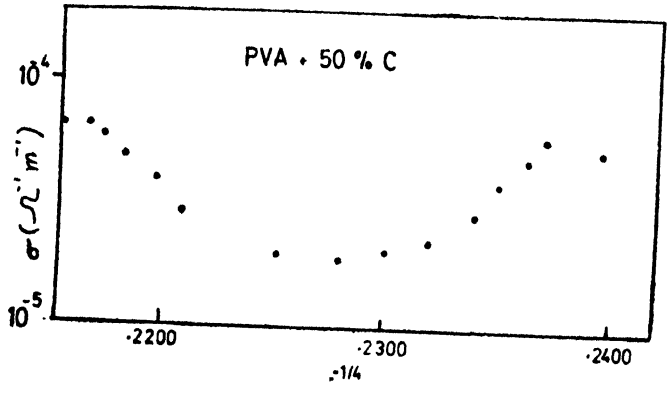

Figure 3. Plot of log σ vs $T^{-1/4}$ for sample PVA+50% C.

due to direct contact between carbon particles or aggregates. Figure 4 represent the plot of log σ vs $T^{-\frac{1}{4}}$ for sample of PVA+50% PVAc. Similar polts might also be drawn for pure PVA, PVA+25% PVAc, and PVA+75% PVAc. We observe that the $T^{-\frac{1}{4}}$ temperature dependence of conductivity seems to fit two straight lines for $T < T_0$ and $T > T_0$. In Table 1, we represent the hopping parameters at two different temperature regions for PVA-PVAc composites. In

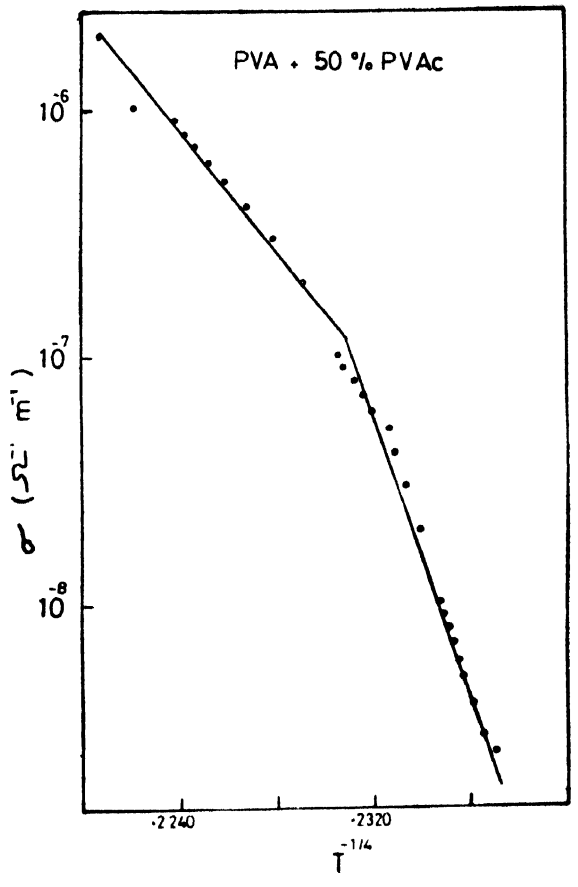

Figure 4. Plot of log σ vs $T^{-1/4}$ for sample PVA+50% PVAc (by weight).

the low temperature region, the exponential term (A) shows anomalous behaviour, yielding unphysical values for R. The cause of this behaviour is not yet clear to us. But in the high temperature region we notice that by increasing PVAc contents, the hopping distance first increases and then decreases. This behaviour is also anomalous because of the fact that the specific conductivity of PVAc is less than the specific conductivity of PVA at the same temperature range. In fact, it is difficult to specify the hopping conduction mechanism alone to represent the conduction in the PVA-PVAc type composites.

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